Electrodeposition of Cu/Ni(Cu) Multilayers from a Citrate Electrolyte in a Flow Cell

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Introduction

Although there have been numerous studies on the mechanical, magnetic and physical properties of metal multilayers. However, most investigators have looked for different combinations of metals, better substrates and appropriate structures, etc, to improve GMR properties. Relatively less attention has been paid to the role of electrochemical parameters such as electrode potential, electrolyte composition and pH, etc. - aspects that may be crucial to the properties of such layers. In this work we have investigated the role of electrochemical parameters on the properties of Cu-Ni(Cu) metal multilayers.

Experimental:

A vertical flow cell was developed for metal multi-layer deposition. Current and potential transients were applied to the electrodes via a potentiostat. The instrumental system was designed to pass different waveforms; pulse currents (PC); pulsed potentials (PP); potential pulse followed by current pulse (PP+CP); pulse currents with a relaxation period (DCP+R). In all experiments, current and potential at the cathode were monitored by a LeCroy oscilloscope. The substrate was a 1 cm diameter glass disc coated with titanium and gold. The size and shape of the substrate (and consequently, that of the electrode holder) were chosen so that they could be directly dismounted from the flow cell and loaded on the stage of the EasyScan® scanning tunnelling microscope.

Electrodeposition Experiments: Cu/Ni(Cu) metal multi-layers of different layer thicknesses were electrodeposited in the flow cell from a citrate electrolyte at pH =6.0 [1,2]. (Cu) indicates that there is a small amount of copper in the Ni layer as impurity. The electrolyte composition was Cu/Ni(Cu) layers was 0.025 M $CuSO_4$ / 0.7 M $NiSO_4$ / 0.25M Na_3Cit. The flow rate was maintained between 40 to 50 cm^3 s^{-1}, which gave a copper diffusion limiting current of 1.0 mA cm^{-2}. Cu/Ni(Cu) multi-layers deposited by PP and CP and PP+CP waveforms produced rough surfaces. However, DCP+R waveforms produced shinier and dense deposits.

A variety of films with different layer thickness and layer compositions were plated; they are shown in Table 1. Thickness and composition of the deposited metal multi-layers were determined by an electron probe microanalysis measurement. Deposit roughness was determined by scanning electron microscopy and scanning tunneling microscopy. Crystal structure of the deposits was determined by x-ray diffraction.

***Results*:** Table 1 lists the Cu and Ni layers plated in the flow cell by PP+CP method. The second and third columns, which are denoted by λ_{Cu}(ex) and λ_{Ni}(ex), are the copper and nickel layer thicknesses expected to form during electrodeposition by simply considering the charge deposited. EPMA measurements were combined with a mathematical model to compute the actual thicknesses of copper and nickel plated, denoted by calc, which are listed in the last two columns. The calculated thicknesses of nickel is substantially lower than expected – this is due to the dissolution of nickel.

Table 1

Q_{Lo} (mC/cm^2)	λ_{Cu} (ex) (Å)	λ_{Ni} (ex) (Å)	$\chi_{Cu,\ EPMA}$	λ_{Cu} (calc) (Å)	λ_{Ni} (calc) (Å)
2.09	7.7	44.0	0.270	7.7	31.6
2.79	10.3	44.0	0.347	10.3	31.6
3.49	12.8	44.0	0.327	12.8	31.6
4.18	15.4	44.0	0.371	15.4	31.6
4.88	17.9	44.0	0.405	17.9	31.6
5.86	21.5	44.0	0.447	21.5	31.6
6.83	25.1	44.0	0.457	25.1	31.6
7.95	29.2	44.0	0.461	29.2	31.6
9.07	33.3	44.0	0.481	33.3	31.6
10.18	37.4	44.0	0.516	37.4	31.6
11.44	42.0	44.0	0.532	42.0	31.6
12.69	46.6	44.0	0.536	46.6	31.6
13.95	51.3	44.0	0.563	51.3	31.6

X-ray diffraction measurements were carried out to determine crystal orientation in the deposits and to detect the appearance of a super-lattice. X-ray diffractograms of Cu/Ni(Cu) layers showed a strong (111) texture, with some visible (110) peaks. This means that the Cu/Ni(Cu) multi-layer is strongly influenced by the substrate, as has been found in many previous studies [3].

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References:

1. T. A. Green, A. E. Russell and S. Roy, *J. Electrochem. Soc.*, **145**, 3, 875 (1998).

2. W. R. A. Meuleman and S. Roy, **PV 99-35** *Fundamental Aspects of Electrochemical Deposition and Dissolution Including Modeling*,, Ed M. Matlosz and D. Landolt, The Electrochemical Society, Inc., Pennington, N.J., USA, (2000).

3. C. Bonhôte, Ph D Thesis, Ecole Polytechnique Federale du Lausanne, Switzerland (1997).